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## (54) Diesel fuel compositions

(57) This invention relates to a diesel fuel composition, comprising a major amount of a diesel fuel and a minor property improving amount of the combination of:

(A) at least one first soluble hydrocarbyl substituted carboxylic acid or acid producing compound, the hydrocarbyl substituent of said first acid or acid producing com-

pound having up to about 24 carbon atoms per molecule; and (B) at least one second hydrocarbyl substituted carboxylic acid or acid producing compound, the hydrocarbyl substituent of said second acid or acid producing compound having at least about 30 carbon atoms per molecule.

#### Description

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This invention relates to diesel fuels and, more particularly, to diesel fuels containing carboxylic acid mixtures.

Low sulfur diesel fuel, defined as having up to 0.05% by weight sulfur content, has been required by law in the U. S. for on-highway use since October 1993 and in Europe since October 1996. Other nations in the Americas and Asia have timetables in place to follow suit. The driving force to low sulfur diesel fuel is the desire to minimize harmful emissions from diesel vehicles. Scientific evidence exists linking diesel fuel sulfur levels to particulate matter emissions from diesel vehicles.

Diesel fuel sulfur level is reduced by hydrotreatment of various distillate streams at the refinery. Hydrotreatment not only removes sulfur, but also removes other polar compounds and polycyclic aromatic compounds normally present in the diesel fuel. These compounds contribute to the natural lubricity of diesel fuel. When these compounds are removed during the hydrotreatment process, the final low sulfur diesel fuel tends to have poor natural lubricity.

Light duty diesel engines are usually fitted with rotary type fuel injection pumps. These pumps are lubricated only by the diesel fuel. Low sulfur fuels having poor natural lubricity have been shown to cause wear in these pumps leading to troublesome operation and premature pump failure. The use of lubricity additives in low sulfur diesel fuels has been shown to reduce or prevent pump wear.

Engine oil contacts diesel fuel in certain types of in-line diesel injection pumps and through direct addition of used engine oil to the fuel. Certain types of lubricity additives used in low sulfur diesel fuel have been found to contribute to fuel filter blockage and to pump plunger sticking. Lubricity additives having poor compatibility with engine oil have been shown to cause these problems. Compatibility is defined as the tendency for the diesel fuel containing the lubricity additive to form fuel insoluble deposits, gels, or heavy sticky residues when in contact with engine oil. These deposits, gels or residues have been shown to cause fuel filter blockage and injection pump sticking.

It would be advantageous to provide a diesel fuel composition that has enhanced lubricity characteristics and is compatible with engine oil. The present invention provides such an advantage.

PCT International Publication No. WO 94/17160 discloses a fuel oil composition comprising a major proportion of a liquid hydrocarbon middle distillate fuel oil having a sulphur concentration of 0.2% by weight or less, and a minor proportion of an additive comprising an ester of a carboxylic acid and an alcohol wherein the acid has from 2 to 50 carbon atoms and the alcohol has one or more carbon atoms.

This invention relates to a diesel fuel composition, comprising a major amount of a diesel fuel and a minor property improving amount of the combination of: (A) at least one first oil soluble hydrocarbyl substituted carboxylic acid or acid producing compound, the hydrocarbyl substituent of said first acid or acid producing compound having up to about 24 carbon atoms per molecule; and (B) at least one second hydrocarbyl substituted carboxylic acid or acid producing compound, the hydrocarbyl substituent of said second acid or acid producing compound having at least about 30 carbon atoms per molecule.

Various preferred features and embodiments of the invention are hereinafter described by way of non-limiting illustration.

As used in this specification and in the appended claims, the terms "hydrocarbyl" and "hydrocarbon based" denote a group having a carbon atom directly attached to the remainder of the molecule and having a hydrocarbon or predominantly hydrocarbon character within the context of this invention. Such groups include the following:

- (1) Hydrocarbon groups; that is, aliphatic, (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl or cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicyclic groups, and the like, as well as cyclic groups wherein the ring is completed through another portion of the molecule (that is, any two indicated substituents may together form an alicyclic group). Such groups are known to those skilled in the art. Examples include methyl, ethyl, octyl, decyl, octadecyl, cyclohexyl, phenyl, etc.
- (2) Substituted hydrocarbon groups; that is, groups containing non-hydrocarbon substituents which, in the context of this invention, do not alter the predominantly hydrocarbon character of the group. Those skilled in the art will be aware of suitable substituents. Examples include halo, hydroxy, nitro, cyano, alkoxy, acyl, etc.
- (3) Hetero groups; that is, groups which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, nitrogen, oxygen and sulfur.

In general, no more than about three substituents or hetero atoms, and preferably no more than one, will be present for each 10 carbon atoms in the hydrocarbyl group.

The term "lower" as used herein in conjunction with terms such as hydrocarbyl, alkyl, alkenyl, and the like, is intended to describe such groups which contain a total of up to 7 carbon atoms.

The term "oil-soluble" refers to a material that is soluble in mineral oil to the extent of at least about one gram per liter at 25°C.

The acid producing compounds of both components (A) and (B) are the anhydrides or partial esters (or partial acids) of such acids. The partial esters are typically half ester and half acid. For example, a partial ester of a substituted succinic acid can be represented by the formula

wherein: R is a hydrocarbyl group; and R1 is a hydrocarbyl group, typically a lower alkyl group.

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The first carboxylic acids and acid producing compounds (A) include oil soluble hydrocarbyl substituted monoand polycarboxylic acids wherein the hydrocarbyl substituent has up to about 24 carbon atoms per molecule, and in
one embodiment about 8 to about 24 carbon atoms, and in one embodiment about 8 to about 22 carbon atoms per
molecule, and in one embodiment about 10 to about 18 carbon atoms. These include fatty acids of up to about 24
carbon atoms, and especially fatty acids having about 10 to about 18 carbon atoms. Examples include saturated and
unsaturated fatty acids, such as palmitic acid, lauric acid, stearic acid, oleic acid, myristic acid, linoleic acid, linolenic
acid, decenoic acid, octadecenoic acid, octadecadienoic acid, 2-ethylhexanoic acid, isooctanoic acid, isodecanoic acid,
neodecanoic acid, tall oil acid, and the like. The acid producing compounds that are useful include the corresponding
anhydrides. When the first carboxylic acid is a polycarboxylic acid, partial esters of such polycarboxylic acids can be
used.

The first carboxylic acids and acid producing compounds (A) include hydrocarbyl substituted succinic acids and anhydrides. These can be represented by the formulae:

wherein in each of Formulae (A-I), R is a hydrocarbyl group of about 8 to about 24 carbon atoms, and in one embodiment about 8 to about 20 carbon atoms, and in one embodiment about 10 to bout 18 carbon atoms. These include tetrapropenyl-substituted succinic acid and anhydride. The production of such substituted succinic acids and their derivatives via alkylation of maleic acid or its derivatives with a halohydrocarbon is well known to those of skill in the art and need not be discussed in detail herein.

Partial esters of the succinic acids or anhydrides represented by Formulae (A-I) can be prepared simply by the reaction of the acid or anhydride with an alcohol or phenolic compound. Particularly useful are the lower alkyl and alkenyl alcohols such as methanol, ethanol, allyl alcohol, propanol, cyclohexanol, etc. Esterification reactions are usually promoted by the use of alkaline catalysts such as sodium hydroxide or alkoxide, or an acidic catalyst such as sulfuric acid or toluene sulfonic acid.

The second hydrocarbyl-substituted carboxylic acids and acid producing compounds (B) are described, for example, in the following U.S. patents, which are incorporated herein by reference: 3,219,666; 3,254,025; 3,271,310; 3,272,743; 3,272,746; 3,278,550; 3,288,714; 3,307,928; 3,346,354; 3,373,111;3,374,174; 3,381,022; and 3,394,179.

The second hydrocarbyl-substituted carboxylic acids (B) are substituted carboxylic acids made by reacting one or more alpha-beta olefinically unsaturated carboxylic acid reagents containing on average from two to about 20 carbon atoms, exclusive of the carboxyl-based groups, with one or more olefin polymers or chlorinated analogs thereof.

The carboxylic acid reagents may be either monobasic or polybasic in nature. When they are polybasic they are preferably dicarboxylic acids, although tri- and tetracarboxylic acids can be used. Exemplary of the monobasic alphabeta olefinically unsaturated carboxylic acid reagents are the carboxylic acids corresponding to the formula:

$$R^{1}$$
— $CH = C$ — $COOH$  (B-I)

wherein in Formula (B-I), R¹ is hydrogen or a saturated aliphatic or alicyclic, aryl, alkylaryl or heterocyclic group, preferably hydrogen or a lower alkyl group, and R² is hydrogen or a lower alkyl group. The total number of carbon atoms in R¹ and R² generally does not exceed about 18 carbon atoms. Specific examples of useful monobasic alpha-beta olefinically unsaturated carboxylic acids are acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, 3-phenyl propenoic acid, alpha, beta-decanoic acid, etc. Exemplary polybasic acids include maleic acid, fumaric acid, mesaconic acid, itaconic acid and citraconic acid.

The alpha-beta olefinically unsaturated carboxylic reagents can also be anhydrides or partial esters of the foregoing acids. A useful alpha-beta olefinically unsaturated carboxylic acid reagent is maleic anhydride. Methods of preparing the partial esters are well known to those of ordinary skill in the art and they can be satisfactorily described by noting the reactants used to produce them. Thus, for example, partial esters for use in the present invention can be made by esterifying monohydric or polyhydric alcohols or epoxides with any of the polycarboxylic acids or acid reagents referred to above.

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The hydrocarbyl substituents of the second carboxylic acids (B) may be derived from olefin polymers or chlorinated analogs thereof. These substituents can be straight chained or branched chained. They typically have an average of at least about 30 carbon atoms per molecule, and in one embodiment an average of at least about 40 carbon atoms, and in one embodiment an average of at least about 50 carbon atoms. In one embodiment, these substituents have an average of from about 30 to about 500 carbon atoms per molecule, and in one embodiment about 40 to about 500 carbon atoms, and in one embodiment about 50 to about 500 carbon atoms.

The olefin monomers from which the olefin polymers are derived are polymerizable olefin monomers characterized by having one or more ethylenic unsaturated groups. They can be monoolefinic monomers such as ethylene, propylene, butene-1, isobutene and octene-1 or polyolefinic monomers (usually di-olefinic monomers such as butadiene-1,3 and isoprene).-Usually-these-monomers-are-terminal olefins, that-is, olefins characterized by the presence of the group > C=CH<sub>2</sub>. However, certain internal olefins can also serve as monomers (these are sometimes referred to as medial olefins). When such medial olefin monomers are used, they normally are employed in combination with terminal olefins to produce olefin polymers which are interpolymers. Although, the hydrocarbyl substituents may also include aromatic groups (especially phenyl groups and lower alkyl and/or lower alkoxy-substituted phenyl groups such as para(tertiary-butyl)phenyl groups) and alicyclic groups such as would be obtained from polymerizable cyclic olefins or alicyclic-substituted polymerizable cyclic olefins, the hydrocarbyl-based substituents are usually free from such groups. Nevertheless, olefin polymers derived from such interpolymers of both 1,3-dienes and styrenes such as butadiene-1,3 and styrene or para(tertiary butyl) styrene are exceptions to this general rule.

Generally the olefin polymers are homo- or interpolymers of terminal hydrocarbyl olefins of about 2 to about 30 carbon atoms, and in one embodiment about 2 to about 16 carbon atoms. A more typical class of olefin polymers is selected from that group consisting of homo- and interpolymers of terminal olefins of 2 to about 6 carbon atoms, and in one embodiment 2 to about 4 carbon atoms.

Specific examples of terminal and medial olefin monomers which can be used to prepare the olefin polymers from which the hydrocarbyl-based substituents are derived include ethylene, propylene, butene-1, butene-2, isobutene, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, pentene-2, propylene tetramer, diisobutylene, isobutylene trimer, butadiene-1,2, butadiene-1,3, pentadiene-1,2, pentadiene-1,3, isoprene, hexadiene-1,5, 2-chlorobutadiene-1,3, 2-methylheptene-1, 3-cyclohexylbutene-1, 3,3-dimethylpentene-1, styrenedivinylbenzene, vinyl-acetate allyl alcohol, 1-methylvinylacetate, acrylonitrile, ethylacrylate, ethylvinylether and methyl-vinylketone. Of these, the purely hydrocarbyl monomers are more typical and the terminal olefin monomers are especially typical.

Often the olefin polymers are polyisobutylenes such as those obtained by polymerization of a C<sub>4</sub> refinery stream having a butene content of about 35 to about 75% by weight and an isobutene content of about 30 to about 60% by weight in the presence of a Lewis acid catalyst such as aluminum chloride or boron trifluoride. These polyisobutylenes generally contain predominantly (that is, greater than about 50 percent of the total repeat units) isobutene repeat units of the configuration

In one embodiment, the hydrocarbyl substituent in the carboxylic acid or acid producing compound (B) as used in the present invention is an alkyl or alkenyl group.

In one embodiment, the carboxylic acid or acid producing compound (B) is a hydrocarbyl substituted succinic acid

or anhydride wherein the hydrocarbyl substituent contains on average about 30 to about 500 carbon atoms, and in one embodiment about 40 to about 500 carbon atoms, and in one embodiment about 50 to about 500 carbon atoms.

The weight ratio of component (A) to component (B) is generally in the range of about 1:99 to about 99:1, and in one embodiment about 30: 70 to about 70:30. In one embodiment, the inventive combination of (A) and (B) is comprised of about 50% to about 99% by weight of (A) and about 50% to about 1% by weight of (B).

The diesel fuels that are useful with this invention can be any diesel fuel. In one embodiment the diesel fuel has a sulfur content of up to about 0.05% by weight as determined by the test method specified in ASTM D 2622-87 entitled "Standard Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry". Any fuel having a boiling range and viscosity suitable for use in a diesel-type engine can be used. These fuels typically have a 90% point distillation temperature in the range of about 300°C to about 390°C, and in one embodiment about 330°C to about 350°C. The viscosity for these fuels typically ranges from about 1.3 to about 24 centistokes at 40°C. These diesel fuels can be classified as any of Grade Nos. 1-D, 2-D or 4-D as specified in ASTM D 975 entitled "Standard Specification for Diesel Fuel Oils". These diesel fuels can contain alcohols and esters.

The inventive diesel fuel compositions contain an effective amount of the combination of components (A) and (B) to improve the lubricity of such diesel fuels and, in one embodiment to improve the compatibility of such diesel fuels with engine oils. The concentration of the combination of (A) and (B) in the inventive diesel fuels is generally in the range of about 10 to about 1000 parts of such combination per million parts of diesel fuel, and in one embodiment about 10 to about 300 parts of such combination per million parts of diesel fuel.

The inventive diesel fuel compositions can contain, in addition to the above-indicated carboxylic acids, other additives which are well known to those of skill in the art. These include dispersants, antioxidants, dyes, cetane improvers, rust inhibitors trialkylamines, bacteriostatic agents, gum inhibitors, metal deactivators, demulsifiers, upper cylinder lubricants and anti-icing agents.

Components (A) and (B) can be added directly to the fuel, or they can be diluted with a substantially inert, normally liquid organic diluent such as naphtha, benzene, toluene, xylene or a normally liquid fuel, to form an additive concentrate. These concentrates generally contain from about 1 % to about 90% by weight of the combination of components (A) and (B). These concentrates may also contain one or more other conventional additives known in the art or described hereinabove.

The following examples are provided to illustrate the invention. Unless otherwise indicated, in the following examples as well as throughout the entire specification and in the appended claims, all parts and percentages are by weight, all pressures are atmospheric, and all temperatures are in degrees Celsius.

### Examples

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In the examples discussed below the following carboxylic acids are used:

A-1: A commercially available fatty acid mixture supplied by Henkel under the trade designation Emersol 210 identified as being a mixture of cis-9-octadecenoic acid (71% by weight), 9,12-octadecadienoic acid (8% by weight), and a mixture of other fatty acids having hydrocarbon chains of 10-22 carbon atoms (21% by weight).

40 B-1: Polyisobutylene (Mn = 940) substituted succinic acid.

In the examples discussed below, the following tests are performed. Ball on Cylinder Lubricity Evaluator (BOCLE) Test: This test measures the adhesive wear aspects (scuffing) of the boundary lubrication properties of diesel fuels on rubbing surfaces. The test is performed using a nonrotating steel ball that is held in a vertically mounted chuck in loaded contact of 7,000 grams with a steel ring rotating axially at 300 rpm. The ring is partially immersed in a sample of the test fluid held at 25°C and in an atmosphere of 50% relative humidity. The mean wear scar diameter on the steel ball after 2 minutes running is used to assess the resistance of the fluid to adhesive wear or its lubricity. The fuel used in each test is kerosene. The results are as follows:

BOCLE Test No. 1:			
	Sample		
	1	2	3
Acid A-1, ppm	0	100	100
Acid B-1, ppm	0	5	0
Mean wear scar diameter, mm	0.61	0.41	0.61

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### EP 0 874 039 A1

BOCLE Test No. 2:			
	Sample		
	1	2	3
Acid A-1, ppm	0	60	60
Acid B-1, ppm	0	4	0
Mean wear scar diameter, mm	0.63	0.53	0.57

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High Frequency Reciprocating Rig (HFRR) Test: This test evaluates the lubricity of diesel fuels. The test involves the use of a 2 ml test specimen of fuel which is placed in the test reservoir of an HFRR and adjusted to a standard temperature (25°C or 60°C). When the fuel temperature has stabilized, a vibrator arm holding a non-rotating steel ball and loaded with a 200 gram mass is lowered until it contacts a test disc completely submerged in the fuel. The ball is caused to rub against the disc with a 1 mm stroke at a frequency of 50 Hz for 75 minutes. The ball is removed from the vibrator arm and cleaned. The dimensions of the major and minor axes of the wear scar are measured and recorded. The diesel fuel is No. 3 grade low sulfur fuel. The results are as follows:

		Sample		
20		1	2	3
	Acid A-1, ppm	0	80	80
	Acid B-1, ppm	0	5	0
•	Wear scar, mm	0.66	0.43	0.50

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Lubricity Improver Compatibility Test: This test is performed using the following procedure:

- (1) A mixture of 50 grams of the combination of Acid A-1 and Acid B-1 (Sample 1) or 50 grams of Acid A-1 (Sample
- 2), 49 grams of diesel engine oil, and 1 gram of water is prepared.
- (2) The mixture from step (1) is stored for 7 days at 80°C.
- (3) The mixture from step (2) is centrifuged for 1 hour at 2000 rpm.
- (4) The sediment formed during step (3) is collected and dissolved in 100 ml of low sulfur diesel fuel.
- (5) The mixture from step (4) is filtered through a 0.8 micron filter and the time for such filtering is recorded with the results being as follows:

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 Sample 1
 Sample 2

 Acid A-1, wt%
 94
 100

 Acid A-2, wt%
 6
 0

 Filter time, seconds
 28.9
 98.0

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While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification.

#### Claims

1. A diesel fuel composition, comprising a major amount of a diesel fuel and a minor amount of a combination of:

(A) at least one first oil soluble hydrocarbyl substituted carboxylic acid or acid producing compound, the hydrocarbyl substituent of said first acid or acid producing compound having up to about 24 carbon atoms per molecule; and

- (B) at least one second hydrocarbyl substituted carboxylic acid or acid producing compound, the hydrocarbyl substituent of said second acid or acid producing compound having at least about 30 carbon atoms per molecule.
- 2. The composition of claim 1 wherein the sulfur content of said diesel fuel is up to about 0.05% by weight.

#### EP 0 874 039 A1

- 3. The composition of claim 1 or claim 2 wherein the hydrocarbyl substituent of (A) has from about 8 to 24 carbon atoms and the hydrocarbyl substituent of (B) has at least about 40 carbons.
- 4. The composition of any preceding claim wherein (A) is at least one of palmitic acid, lauric acid, stearic acid, oleic acid, myristic acid, linoleic acid, linolenic acid, decenoic acid, octadecenoic acid, octadecadienoic acid, 2-ethylhexanoic acid, isooctanoic acid, isodecanoic acid, neodecanoic acid, tall oil acid, and tetrapropenyl substituted succinic acid or anhydride.
- 5. The composition of any preceding claim wherein (A) is cis-9-octadecenoic acid, 9,12-octadecadienoic acid or a mixture thereof.
  - 6. The composition of any preceding claim wherein components (A) and (B) are independently an anhydride or partial ester.
- 7. The composition of any preceding claim wherein the hydrocarbyl substituent of component (B) has at least about 40 carbon atoms.
  - 8. The composition of any preceding claim, wherein component (B) has the formula

wherein R is a hydrocarbyl group.

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- 9. The composition of claim 8 wherein R is derived from a polyisobutylene.
- 10. A diesel fuel composition, comprising a major amount of a diesel fuel having a sulfur content of up to about 0.05% by weight and a minor amount of:
  - (A) at least one fatty acid; and
  - (B) at least one polyisobutylene substituted succinic acid,

the polyisobutylene group of said succinic acid having an average of at least about 50 carbon atoms per molecule.



# **EUROPEAN SEARCH REPORT**

Application Number EP 98 30 3110

Category	Citation of document with in of relevant passa	dication, where appropriate, ages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL6)
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X	* column 7, line 25 * column 8, line 50	- line 37 *	1,2,4,5, 8	
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	The present search report has be			·
	THE HAGUE	Date of completion of the search		Examiner
CA X : partic Y : partic docus A : techs O : non-	ATEGORY OF CITED DOCUMENTS cutarly relevant if taken alone cutarly relevant if combined with another ment of the same category notogical background written disclosure mediate document	L : document cited to	underlying the ument, but public the application of other reasons	ished on, or

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